Appendix A

Zero Discharge Demonstration Program Pollutants, Lake Superior Critical, and Prevention Pollutants (Organics): How Are These Chemicals Used?

A.1 Introduction

Nine chemicals were named in the Binational Program for the Lake Superior Zero Discharge Demonstration Program (ZDDP). For five of the chemicals, mercury, polychlorinated biphenyls (PCBs), dioxin, hexachlorobenzene (HCB), and octachlorostyrene (OCS), a number of uses contribute(d) loads of pollutants to the environment. The uses of these chemicals are described and graphically depicted in Section A.2.

The remaining four ZDDP chemicals were used as pesticides: DDT, chlordane, dieldrin, and toxaphene. These organic chemicals are easily volatilized and carried into the atmosphere. The past uses of these chemicals are briefly described in Section A.3. Since the production and use of these chemicals have been banned by both the United States and Canada, and since no known uses currently exist, no use trees were developed for these chemicals.

A.2 Non-Pesticide ZDDP Pollutants

The following sections contain information regarding the historical and present use and sources of the five non-pesticide ZDDP pollutants.

A.2.1 Mercury

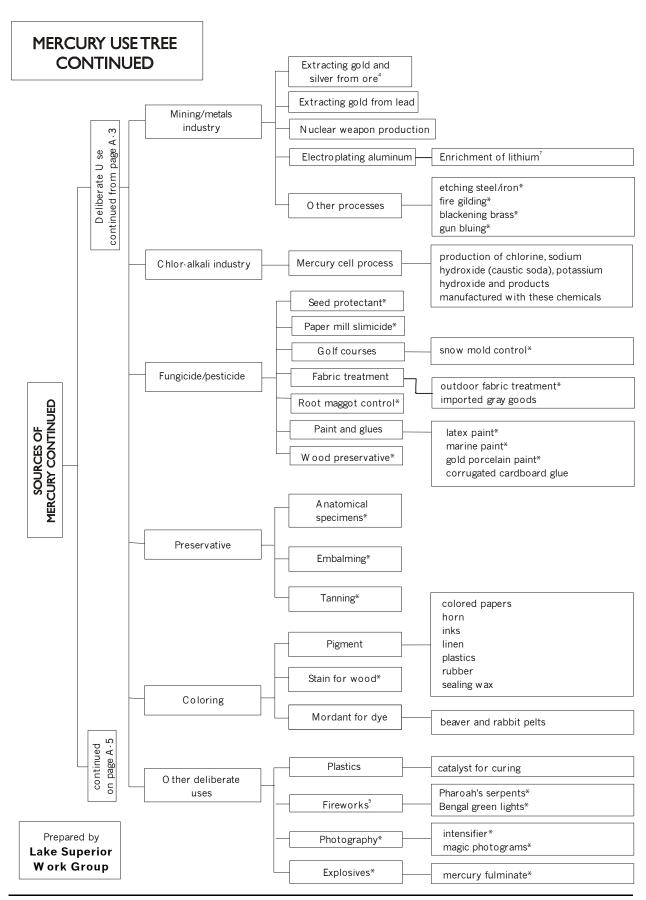
Mercury is included in the Zero Discharge Demonstration based on its toxicity to humans and wildlife, its impact on beneficial uses for Lake Superior, and its wide range of sources both inside and outside the Lake Superior basin (See Mercury Use Tree). Although mercury is a naturally-occurring element, its use in various products and applications results in environmental releases. Examples of products containing mercury include: thermometers, batteries, electrical switches, pigments, and preservatives. Applications of mercury include electroplating, ore extraction, and electrolysis. Mercury is also released in combustion, mining, and manufacturing.

A.2.2 PCBs

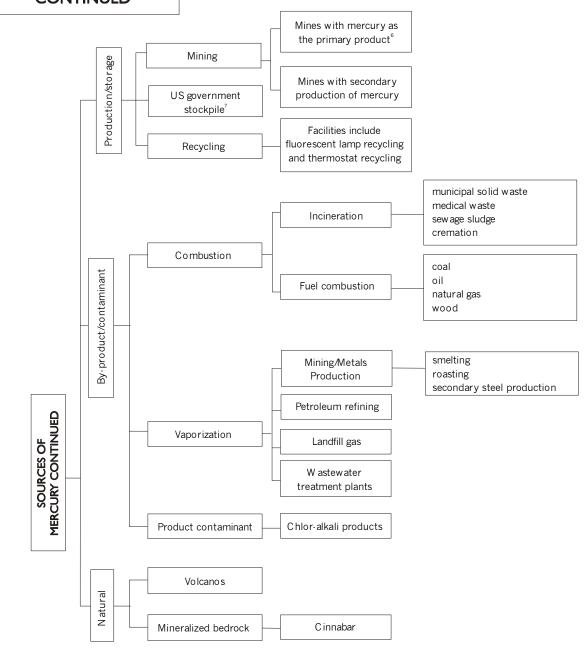
PCBs are in the Zero Discharge Demonstration based on its toxicity to humans and wildlife, its persistence and bioaccumulative properties, and its impact on beneficial uses of Lake Superior. Although PCBs were banned in 1979, there are an estimated 340,000 tons still in use in the United States and Canada (See PCB Use Tree). While PCBs had a wide variety of uses, most of the PCBs still in use serve as coolant insulation fluids in electrical transformers and capacitors. PCBs were sold under the trade names of Aroclor, Askeral, and PCB Askarel.

A.2.3 Dioxin

Dioxin is a Zero Discharge chemical because of its high toxicity, its impact on beneficial uses for Lake Superior, and its wide range of sources (see Dioxin Use Tree). Dioxin is created by a variety of processes, including some natural processes. U.S. Environmental Protection Agency's dioxin reassessment document identifies four major sources of dioxin:



MERCURY USE TREE CONTINUED



^{*} Use is known or assumed to be discontinued.

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¹ Use has been discontinued in new equipment but old equipment may still be in use.

 $^{^{\}rm 2}{\rm These}$ products are banned in some jurisdictions.

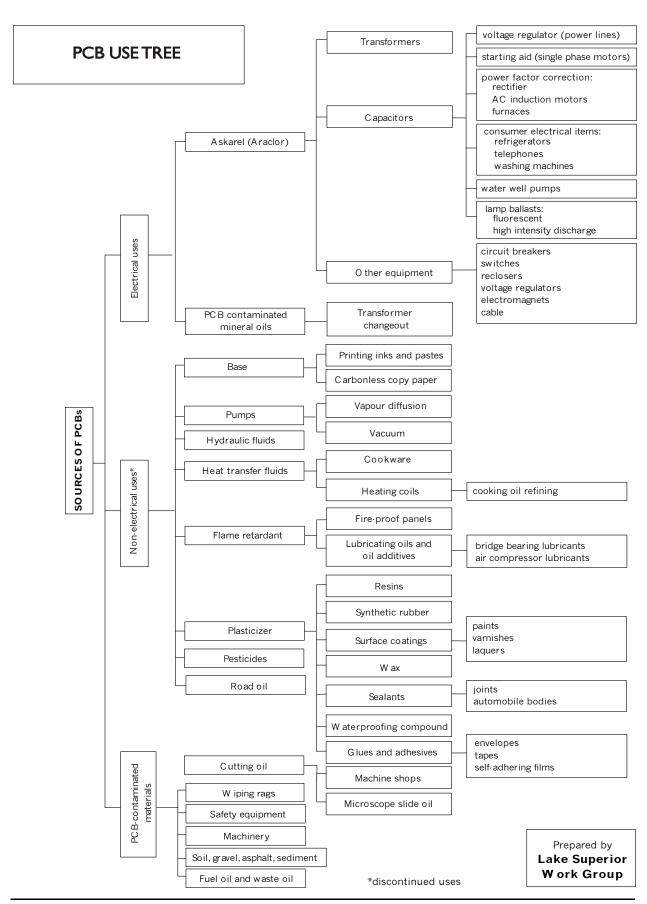
 $^{^{\}mbox{\tiny 3}}$ C aribbean, C hinese, C entral America, possibly Hmong.

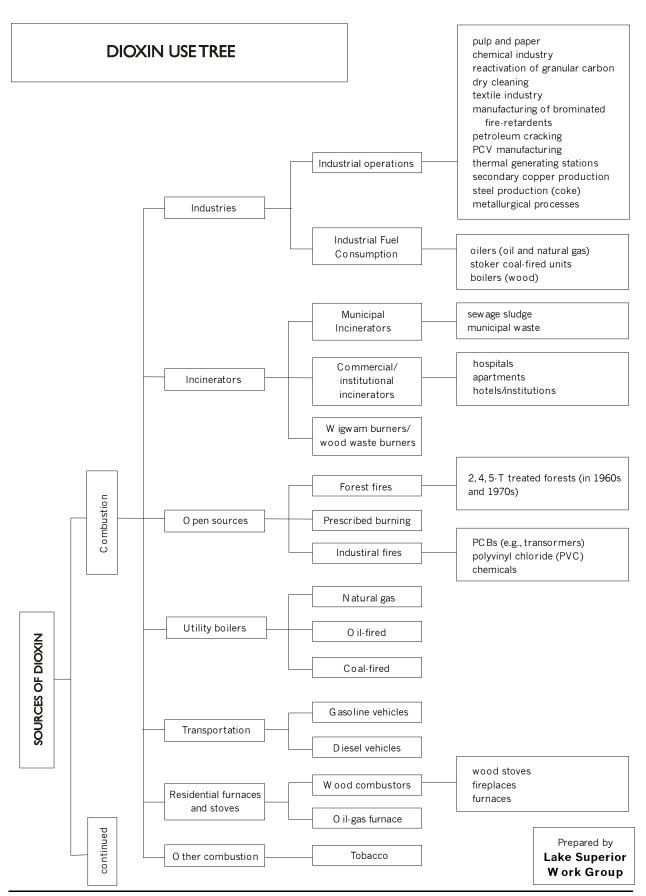
⁴ Use of mercury for gold and silver mining is discontinued in the US and Canada, except for recreational mining; use of mercury for commercial gold mining continues elsewhere (e.g., Brazil).

 $^{^{\}scriptscriptstyle 5}$ Fireworks made in the US no longer contain mercury but imported fireworks may.

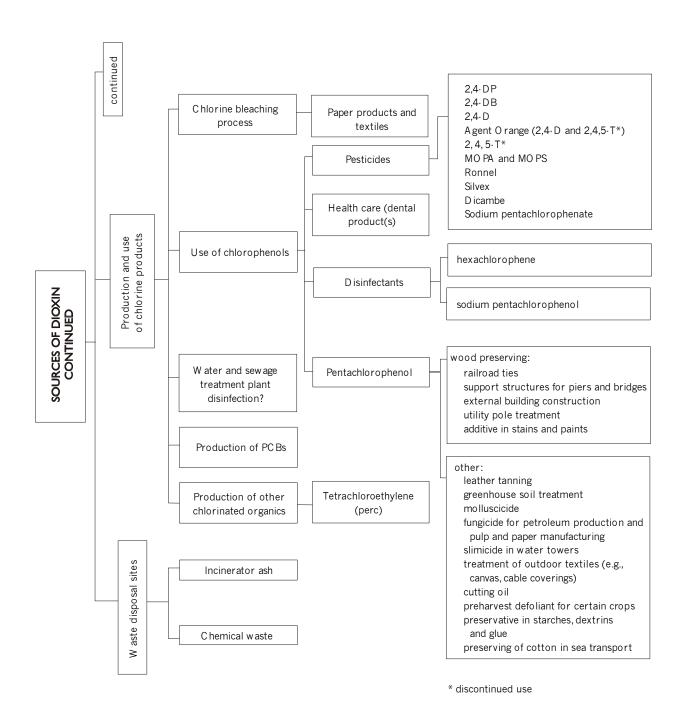
⁶ Mercury mines existed in the US and C anada but have discontinued due to the market and environmental regulations. Globally, mercury mines continue to operate.

⁷ The USD epartment of D efense suspended sales in 1994 and is consulting with EPA.





DIOXIN USE TREE CONTINUED



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HEXACHLOROBENZENE (HCB) USE TREE production of aromatic fluorocarbons (e.g., hexafluorobenzene) O rganic synthesis PCP manufacture (European method) Plasticizer for vinyl chloride chemical intermediate for dyes Raw material Ammunition and pyrotechnic additive* peptizing agent for nitrose and styrene Synthetic rubber* Manufacturing type rubbers (auto tires) wheat Fungicide sunflower other small grains Wood preservative* Veterinary use* treatment of wireworms Product Preservative for paper* SOURCES OF HEXACHLOROBENZENE (HCB) Results from use of PCP as a preservative for cotton* KNOWN SOURCES** carbon tetrachloride industrial chemical pentachlorobenzene manufacture tetrachloroethylene (perc) trichloroethylene KNOWN SOURCES*** dichloram Pesticide dimethyltetrachloroterephthalate (dacthal) manufacture lindane (HCB is a metabolite) By-product m-tetrachlorophthalonitrile (chlorothaionil) A luminum manufacture* pentachlorobenzene (PCNB) pentachloronitrobenzene pentachlorophenol Electrode manufacture* chlorine Electrolysis caustic soda sodium metal Nonferrous metal manufacturing Combustion Incineration of Flue gases and titanium dioxide sludge and solid fly ash waste Prepared by Lake Superior Work Group

HEXACHLOROBENZENE (HCB) USE TREE CONTINUED

* DISCONTINUED USE

** SUSPECTED SOURCES (INDUSTRIAL CHEMICALS)

Chlorinated solvents:

hexachloroethane

I, I, 2-trichloro-I, I, 2-trifluoroethane

I, I, 2-trichloroethane

ethylene dichloride

chlorinated biphenyls

chlorinated naphthalene

chlorobenzenes

dichloropropenes

Chlorinated monomers:

vinyl chloride

2-chlorobutadiene

Chlorinated intermediates:

phosgene

hexachlorocyclopentadiene

allyl chloride

cyuranic chloride

tetrachlorophthalic anhydride

Other chemical production:

titanium dioxide

toluene diisocyanate

reactive azo dyes from cyanuric chloride

phthalocyanine dyes and pigments

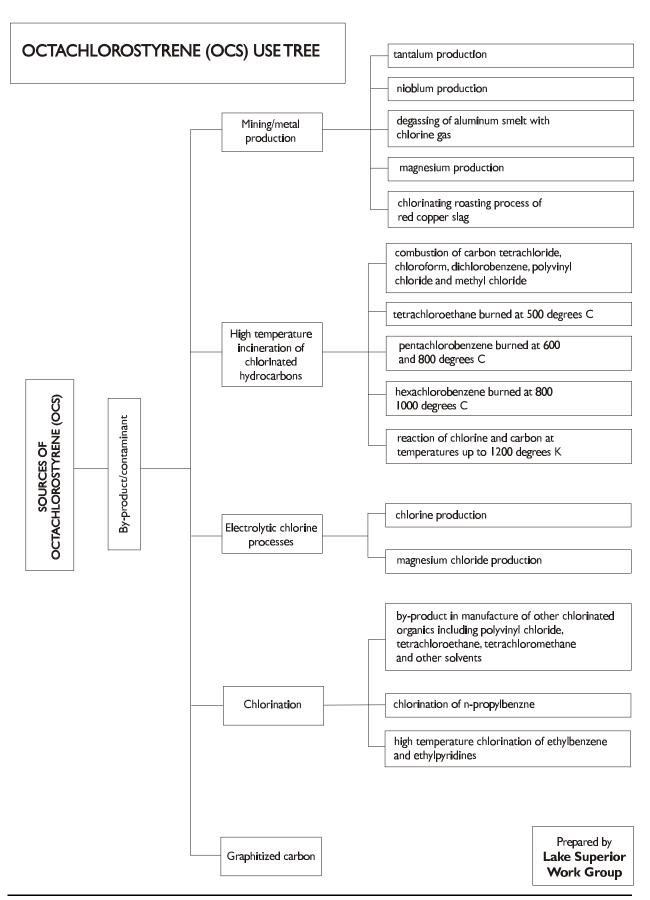
*** SUSPECTED SOURCES (PESTICIDES)

Pesticides derived from 1,2,4,5-trichlorobenzene (e.g., 2, 4, 5-T, Silvex and others)
Trichlorobenzene and derivatives (e.g., 1, 2, 4-trichlorobenzene)
Trichlorotoluene derivatives (e.g., 2, 3, 6-trichlorobenzolc acid and 2, 4, 5-trichlorobenzene acetic acid)
Chlorophenol derivatives (e.g., pentachlorophenol and 2, 4, 6-trichlorophenol)

S-Triazine derivatives (e.g., atrazine, propazine and simazine)
Chlorinated-cyclopentadiene derivatives (e.g., chlordane, endosulfan, endrin, heptachlor and mirex) miscellaneous

For a more complete listing, see Morris and Cabral (eds.), 1986

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A.3 ZDDP Pollutants Used as Pesticides

The following sections contain information about the past uses of the four pesticide ZDDP pollutants.

A.3.1 Chlordane

Chlordane was used for the control of ants and other insects on corn, grapes, strawberries, and other crops. It was also used by veterinarians to control fleas, lice, ticks, and mange. Most uses of chlordane were banned in the United States in 1978. Use of chlordane as a termiticide was halted in 1988 pending air monitoring tests. In Canada, registration of chlordane was discontinued in 1990.

A.3.2 DDT

DDT was used as a pesticide against the Japanese beetle, spruce bud worm, gypsy moth, codling moth, and Dutch Elm Disease bark beetle. It was used heavily in cotton fields in the United States and during WWII to control outbreaks of typhus. In addition to the use of pure DDT, it also made up 15% of the pesticide Dicofol. This pesticide was used on citrus and apple crops, as well as on other fruit trees and ornamental plants. In the U.S., the use of DDT was canceled in 1973 and Dicofol was banned in 1988. In Canada, registration of DDT was discontinued in 1985.

A.3.3 Dieldrin

Dieldrin was used widely from 1950 to 1974 for soil-dwelling insects, especially termites. It was also used on cotton, corn, and citrus crops. Other uses included locust control, vector control, fire ant control, wood preservative, and moth-proofing wool products. All uses of dieldrin in the United States have been canceled or suspended. In Canada, registration of dieldrin was discontinued in 1990.

A.3.4 Toxaphene

Toxaphene was used as a pesticide against army worms, bollweevil, boll worm, cotton aphid, cotton fleahopper, cotton leafworm, grasshopper, rapid plant bug, and thrips. Large amounts of toxaphene were used in the southern United States to control pests on soybeans, cotton, and grain. It was also used as a cattle dip. All uses of toxaphene were canceled in the United States in 1982. In Canada, the pesticide use of toxaphene was suspended in 1980.

A.4 Uses of Prevention and Remediation Lakewide Management Category Chemicals

Uses are described for a number of additional organic chemicals that fall into the remediation and prevention management categories (see Table A-1). These chemicals include BHC, 2-chloroaniline, 3,3'-dichlorobenzidine, 1,4-dichlorobenzene, heptachlor/heptachlor epoxide, hexachlorobutadiene, mirex/photomirex, PAHs, pentachlorobenzene, pentachlorophenol, 1,2,3,4-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, and tributyl tin.

Table A-1. Lake Superior Prevention and Remediation Lakewide Chemicals (Organics)

Chemical	LaMP Category	Sources	Other names
BHC ¹ , alpha	Remediate: Lakewide	Toxic hexachlorocyclohexane isomer found in BHC and technical Lindane (see BHC)	alpha hexachloro- cyclohexane
BHC ^{1,2} , beta and delta and congeners	Prevention: Investigate	Insecticide for rice; seed treatment for cereals, sugar beets and rapeseed; used against cockroaches, flies, aphids, grain weevils and beetles; scabicide ointment for human use; veterinary use for external parasites; BHC (except for gamma-BHC [Lindane]) was canceled in 1978	hexachlorocyclo- hexane, HCH, benzene hexachloride
2-chloroaniline	Prevention: Investigate	Used in making synthetic rubber parts as well as epoxy resin, urethane foam padding, gun mounts, jet engine turbine blades, radar systems and components in some home appliances	4,4'-methylenebis
3,3'- dichlorobenzidine ³	Prevention: Investigate	Used in manufacture of pigments (azo dyes) for printing ink, textiles, plastics and crayons; intermediate for Benzidine Yellow pigments; curing agent for solid urethane plastics	
1,4-dichlorobenzene	Prevention: Monitor	Fumigant used for control of clothes moth and mildew and mold on leather and fabrics; air deodorant (including urinal deodorizers); by-product in manufacture of monochlorobenzene	para- dichlorobenzene; PDB
heptachlor/ heptachlor epoxide ¹	Remediation: Lakewide	Termiticide, used against Japanese beetle, fire ants, boll weevil and soil insects; most uses canceled; certified applicators can use it on pineapples and sugarcane; use as termiticide in US halted pending testing; contaminant in chlordane	
hexachlorobuta-diene	Prevention: Investigate	Solvent for elastomers (rubberlike polymers), heat transfer fluid, transformer and hydraulic fluid, wash liquor for removing higher hydrocarbons	
mirex/photo mirex	Prevention: Monitor	Insecticide (particularly effective against fire ants and cockroaches); fire retardant for plastics, rubber, paint, paper and electrical goods; 25% of the 3.3 million pounds produced in the US were used for pesticide, remainder used as fire retardant; all registered uses in US were canceled in 1977; banned in 1994 in Ontario; never registered or used in Canada by the agriculture industry.	chlordecane
PAHs	Remediation: Lakewide	benzo[a]pyrene is the most toxic of the PAHs; naphthalene is used in production of phthalic acid; PAHs are found in petroleum products (e.g., creosote and asphalt) and formed during incomplete combustion; sources include heat and power generation, cigarettes, refuse burning, industrial activity (i.e., coke ovens and aluminum smelting), coal refuse heaps; can be formed naturally in forest fires; transportation accounts for 1% of PAHs emitted nationwide, but may account for 50% of urban PAH exposure	polynuclear aromatic hydrocarbons, PNAs, POMs; benzo[a]pyrene is also known as BAP

Table A-1. Continued.

Chemical	LaMP Category	Sources	Other names
pentachlorobenzene	Prevention: Monitor	precursor and impurity in soil fungicide pentachloronitrobenzene; also used as a fire retardant and in dielectric fluids; there is no Canadian production or demand for pentachlorobenzene; Lindane degrades to pentachlorobenzene	
pentachlorophenol	Prevention: monitor	preservative/termiticide for wood; preservative for starches, dextrins and glues; major use (90%) was as a wood preservative; 9% went to production of sodium pentachlorophenate; PCP and Na-PCP together were formerly the second most used pesticide in the US as preharvest defoliant for cotton and as a general herbicide; Na-PCP used for marine anti-fouling paint, cooling tower disinfection, fungicide in textiles and general disinfectant; PCP is a breakdown product from HCB and pentachlorobenzene	PCP
1,2,3,4- tetrachlorobenzene	Prevention: Monitor	no known production (circa 1988) in the US; has been used in dielectric fluids; no known current uses in Canada	
1,2,4,5- tetrachlorobenzene	Prevention: Investigate	used as a chemical intermediate (e.g., used to make 2,4,5-T and other organic chemicals); used in the dye industry; used in moisture-proofing electrical insulation	
tributyl tin	Prevention: Investigate	antifoulant; preservative in adhesives, leather, glass, paint, paper and wood; antifouling uses of tributyl tin were eliminated in Ontario in 1989	

Sources: A Compendium of Information on Pesticides Used in the Atlantic Region EC, 1990); CEPA Assessment Reports (E.C.); COA Pesticide Review; Farm Chemicals Handbook (1990); Handbook of Toxic and Hazardous Chemicals and Carcinogens (1985); Merck Index (1983); National Study of Chemical Residues in Fish, Vol. II (EPA, 1988)

See pesticide straw paper.
 Technical grade Lindane is a mixture of HCH isomers.
 No substitutes for many of its uses.